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Adsorption Behavior of CH₄ Gas Molecule on the MoX₂(S, Se, Te) Monolayer: The DFT Study

Jian Ren^{1*} , Hui Liu², Yanyan Xue¹ and Lin Wang¹

Abstract

We predict the CH₄-sensing performance of monolayer MoX₂(S, Se, Te) with X-vacancy, Mo-vacancy, and divacancy by the density functional theory (DFT). The results demonstrate that the combination of different sixth main group elements with Mo atom has different adsorption behaviors for CH₄ gas molecule. Compared with MoX₂, MV_X, MV_{Mo}, and MV_D generally exhibit better adsorption properties under the same conditions. In addition, different defects will have different effects on adsorption behavior of the systems, the MV_D(MoTe₂) has the better adsorption, the better charge transfer, and the shortest distance in these systems. The results are proposed to predict the CH₄ gas molecule adsorption properties of MV_D(MoTe₂) and would help in guiding experimentalists to develop better materials based on MoX₂ for efficient gas detection or sensing applications.

Keywords: CH₄ gas molecule, Monolayer MoS₂, Band gap, DFT, Charge transfer, Adsorption energy, Sensor

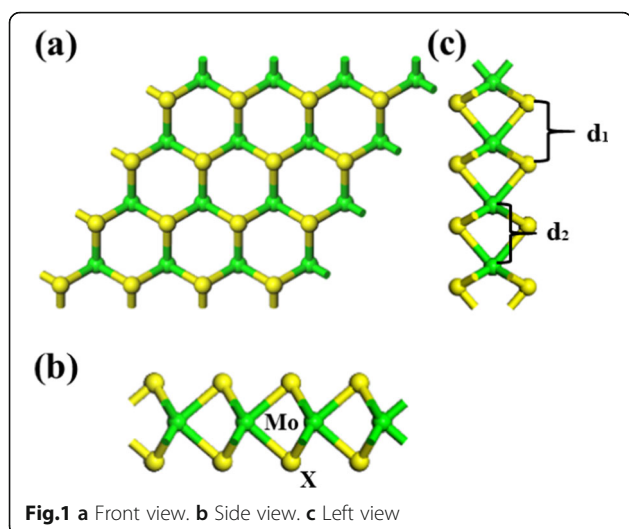
Introduction

Methane (CH₄) is the simplest organic compound with colorless and tasteless gas [1–4], which is basically non-toxic to human beings, the oxygen content in the air will obviously decrease when the concentration of methane is too high, which makes people suffocate. When the concentration of methane reaches 25–30% in the air, it will cause headaches, dizziness, fatigue, inattention, rapid breathing and heartbeat, and ataxia [5–7]. Since the rise of graphene [8, 9] and the discovery of topological insulators [10], a lot of interesting physics have been found in systems with reduced dimensions. Other two-dimensional (2D) material, such as monolayers or few-layer systems (nanolayers) of transition-metal dichalcogenides (TMDs), gain importance because of their intrinsic band gap [11–15]. TMDs are MX₂-type compounds where *r*(S, Se, Te) [16–19]. These materials form layered structures in which the different *X-M-X* layers are held together by weak van der Waals forces [20–26]. Yi Li [27] studied that the adsorption energy of COF₂ on Ni-MoS₂ was better than CF₄, and Ni-MoS₂ acted as electron donor and obvious charge

transfer was observed. Soumyajyoti Haldar [28] reported that structural, electronic, and magnetic properties of atomic scale defects in 2D transition metal dichalcogenides MX₂, and different vacancy had a great effect on different 2D dichalcogenides MX₂, it is likely that band gap, density of states, some properties, and so on. Janghwan Cha [29] used different functionals to show the relatively binding energies about gas molecule and MoX₂. The optPBE-vdW functionals showed relatively large binding energies. Furthermore, the TMDs are promising materials to realize gas sensors, so we study the effect of many defects on MoX₂(X=S, Se, Te) for structure, band gap [30–32], adsorption energy, charge transfer, etc. This paper studied the interaction of methane with monolayer MoX₂ by first-principle simulation (see Fig. 1). The green color ball is Mo atom, and the yellow color ball is X atom, the distance of *d*₁ for S-S, Se-Se, and Te-Te is 3.190 Å, 3.332 Å, and 3.559 Å, respectively, the distance of *d*₂ is the same as the three cases of *d*₁. This work was based on DFT, and the adsorption energy, charge transfer, adsorption distance, and density of states (DOS) of CH₄ gas molecule on MoX₂ were studied.

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Method and Theory

A 4×4 supercell of MoX_2 (32 X atoms and 16 Mo atoms) and CH_4 gas molecule adsorbed onto it was built in Materials studio [33–36]. DMol³ [37] software was used for calculation. In this paper, the Perdew, Burke, and Ernzerhof (PBE) [38, 39] functions with generalized gradient approximation (GGA) were selected to describe the exchange energy Vxc. The Mo was generated in $4p^6 5s^1 4d^5$ configuration and another was used for the generation of the valence electrons of X. The Brillouin zone of MoX_2 was sampled using a $6 \times 6 \times 1$ k-point grid and Methfessel-Paxton smearing of 0.01 Ry. The

cutoff energy was 340 eV with self-consistence-field (SCF) converged of 1.0×10^{-5} eV. All the atomic structures were relaxed until the maximum displacement tolerance of 0.001 Å and maximum force tolerance of 0.03 eV/Å [40, 41].

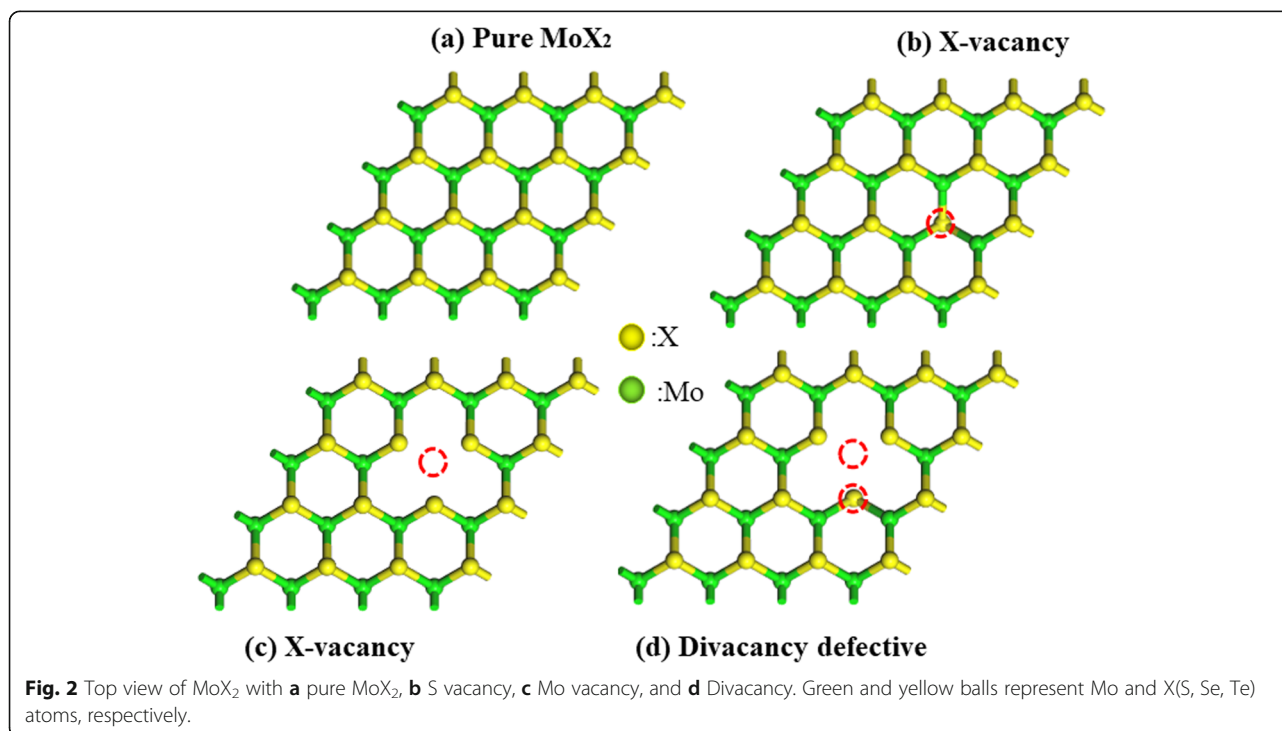
We calculated the adsorption energy (E_{ad}) in the adsorbed systems, which was defined in the following equation:

$$E_a = E_{\text{MoX}_2 + \text{CH}_4 \text{ gas molecule}} - (E_{\text{MoX}_2} + E_{\text{CH}_4 \text{ gas molecule}})$$

Where, $E_{\text{MoX}_2 + \text{CH}_4 \text{ gas molecule}}$, E_{MoX_2} and $E_{\text{CH}_4 \text{ gas molecule}}$ represent the energies of the monolayer MoX_2 adsorbed system, monolayer MoX_2 , and a CH_4 gas molecule, respectively. All energies achieve the best optimization after structural optimization. We used Mulliken's population analysis to study the charge transfer.

Results and Discussion

Firstly, we discussed the geometric and electric structures of the four MoX_2 substrates (see in Fig. 2). The bond length of Mo-S, Mo-Se, and Mo-Te were 2.426 Å, 2.560 Å, and 2.759 Å, which were in good agreement with experimental value of 2.410 Å (MoS_2) [42, 43], 2.570 Å (MoSe_2) [44] and 2.764 Å (MoTe_2) [45], the four structures MoX_2 were in this paper, pristine MoX_2 , MV_X (one X atom vacancy), MV_Mo (one Mo atom vacancy), and MV_D (one X atom and one Mo atom vacancy) respectively. Full structural relaxation showed that the stretching X-Mo bond length from 2.420 Å to



2.394 Å (MV_S), 2.420 Å to 2.398 Å (MV_{Mo}), and the main reason was that the absence of atoms enhanced the interaction between the adjacent Mo atoms and other S atoms, the chemical bond became stronger and the bond length became shorter.

Figure 3a–c displayed the calculated adsorption energy, charge transfer, and adsorption distance of CH_4 /MoX₂ system. Before the adsorption, the distance between the CH_4 gas molecules and the molybdenum disulfide was 3.6 Å. The CH_4 gas molecule obtained about -0.001 e to -0.009 e from the four systems of MoS₂ sheet, -0.009 e to -0.013 e from the four systems of MoSe₂ sheet and -0.014 e to -0.032 e from the four systems of MoTe₂ sheet, respectively, which means that CH_4 acted as an acceptor. Inclusion of the van der Waals correction enhances the adsorption energies of CH_4 gas molecule by -0.31 eV to -0.46 eV on the four systems of MoS₂ systems, by -0.07 eV to -0.50 eV on the four systems of MoSe₂ systems, and by -0.30 eV to -0.52 eV on the four systems of MoTe₂ system, and 0.01 eV was usually thought within the error range. It was obvious that the adsorption distance was the shortest in the case of S atom defects and divacancy defects. To sum up the above data, we saw that the adsorption effect was the best under the condition of divacancy defect.

Adsorption of CH_4 Gas Molecule on Monolayer MoS₂

In order to have a clear understanding about the bonding mechanism of CH_4 gas molecule on pure and defected MoS₂ (including MV_S , MV_{Mo} , and MV_D), we analyzed the corresponding density of states (DOS) for adsorbed CH_4 gas molecule in adsorption structures. Comparing four systems, the adsorption effect of CH_4 gas molecule on pure and defected MoS₂ (including MV_S , MV_{Mo} , and MV_D) were further investigated. The DOS (Fig. 4) showed that there was a certain change in the vicinity of the Fermi level, which was the same as the general DOS form. The energy band gap of four systems was observed along the gamma point (G) noticed to be 1.940 eV (MoS₂), 1.038 eV (MV_S), 0.234 eV (MV_{Mo}), and 0.209 eV (MV_D). Moreover, the observed energy band gap of MoS₂ nanosheet was in good agreement with other reported theoretical work (1.78 eV [39], 1.80 eV [40]) and experimental work (1.90 eV [41], 1.98 eV [42]). Meantime, monolayers MoS₂ had five peak values, the peak was -12.2 eV, -5 eV, -4 eV, -2 eV, and -1 eV which were ascribed to the S atom in MoS₂ and the Mo atom in MoS₂. However, the DOS of four systems (Fig. 4) showed that the electronic level of CH_4 gas molecule has a peak for about -3 eV which was closed to Fermi level. It was contributed to the conduction band in the system and affects the conductivity of

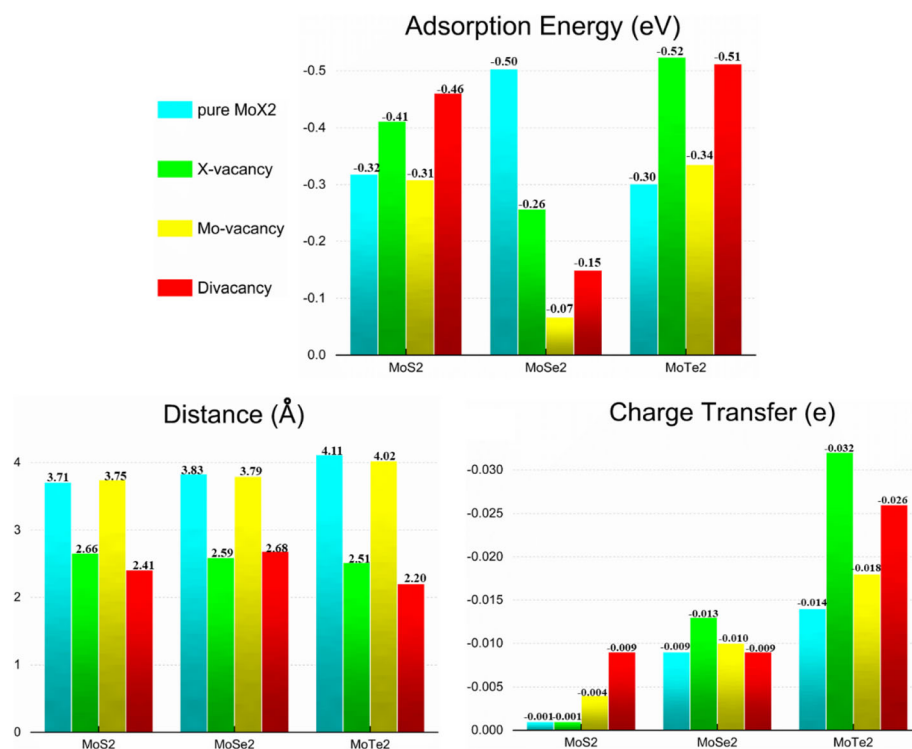


Fig. 3 Adsorption energies, shortest atomic distances between molecule and MoX₂, and charge transfers

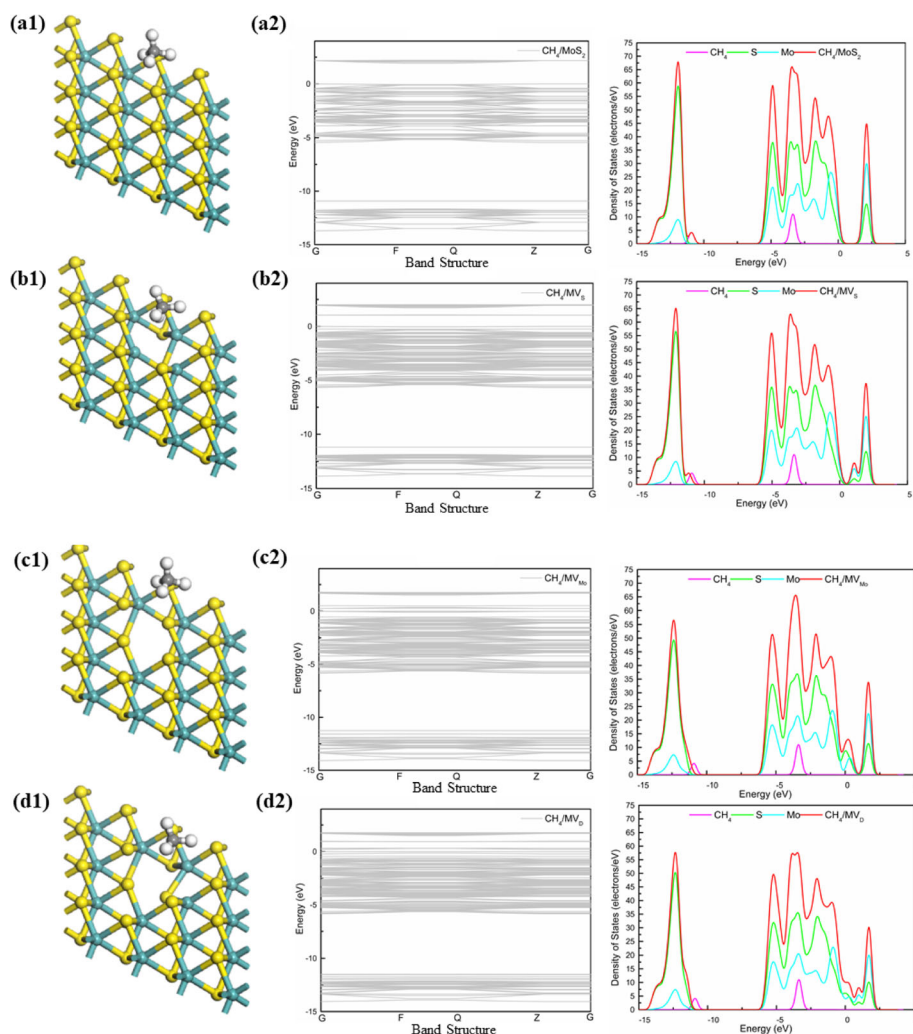


Fig. 4 The structure and DOS of CH₄ gas molecule on four systems (MoS₂, MVSe, MVMo, and MVTe)

the system. Comparing four systems, the peak of -12.5 eV MVs was obviously much lower than MoS₂ because of the defect of the S atom in the MoS₂. And the defects of the Mo atom do not have much effect; however, the contribution at the conduction zone was still decreasing. As shown in Fig. 3 b, obviously, the band around the 0 eV was getting smaller and smaller, and the curve was more and more stable. In summary, there was no bond between CH₄ gas molecule and MoS₂, and the electron transfer and adsorption energy were small, and the adsorption was not very strong, which was obviously physical adsorption.

Adsorption of CH₄ Gas Molecule on Monolayer MoSe₂

We studied the adsorption of CH₄ gas molecule on four systems of MoSe₂, it could be seen from the DOS (Fig. 5) that the electron energy levels of CH₄ gas molecule in the four adsorption orientations were close to the Fermi level, which had a certain influence on the conductivity of the

system, and the band gap system was so small, same as adsorption of MoS₂. Meantime, the DOS (Fig. 5) also showed that the Se atoms in MoSe₂ had five peak values, the peak was -12 eV, -5 eV, -4 eV, -3 eV, and -2 eV, the Mo atom in MoSe₂ had overlapping peaks at about 0.5 eV and 2 eV. Compared with MoS₂, Se contributed more to the system than S in MoS₂ below the Fermi level, and the energy band gaps of four systems were observed along the gamma point (G) that was noticed to be 1.680 eV (MoSe₂), 1.005 eV (MVSe), 0.094 eV (VMo), and 0.024 eV (MVTe). The band was narrower and more stable around the 0 eV. Therefore, it could be confirmed that the adsorption properties and the CH₄ gas molecule on the four systems were physisorption.

Adsorption of CH₄ Gas Molecule on Monolayer MoTe₂

We studied the adsorption of CH₄ gas molecule on four systems of MoTe₂, the DOS (Fig. 6) of CH₄ gas molecule on the MoTe₂ were analyzed. As shown in Fig. 6, the

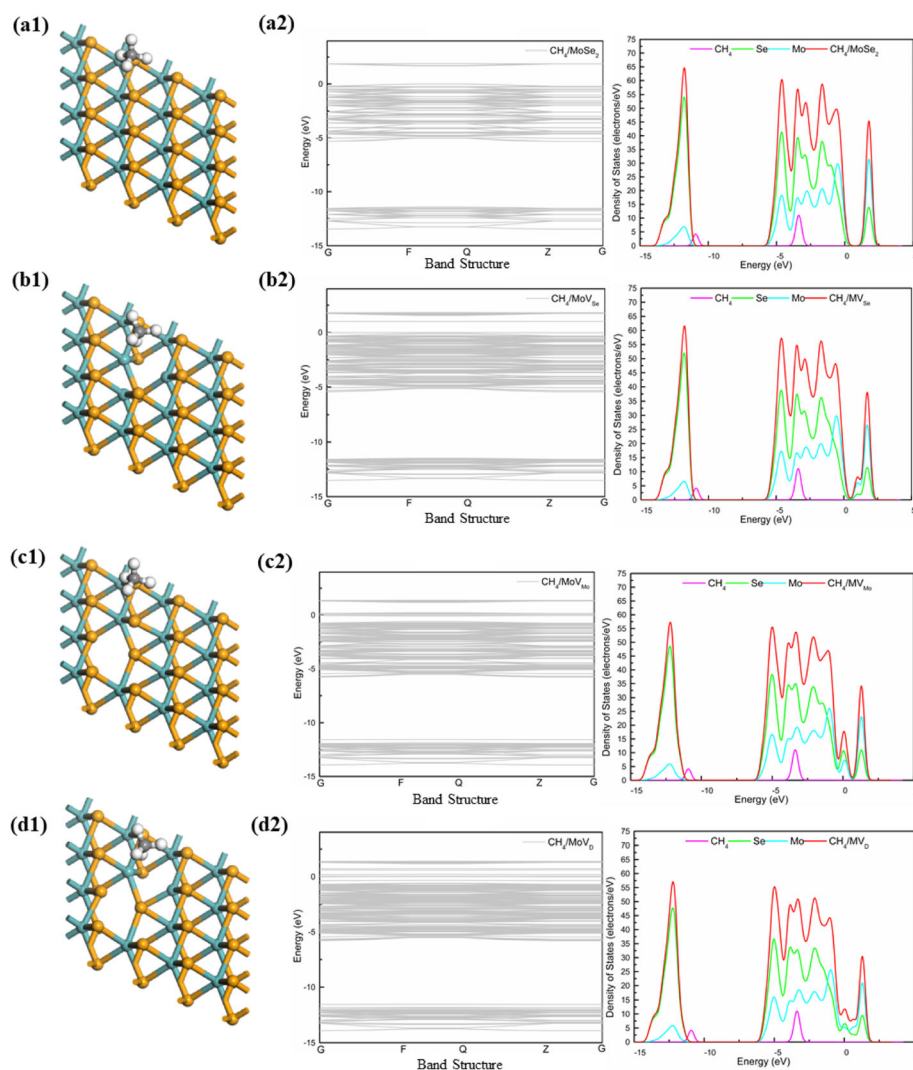


Fig. 5 The structure and DOS of CH₄ gas molecule on four systems (MoSe₂, MVSe, MVMo, and MVTe)

electronic levels of CH₄ in the four MoTe₂ systems were short with CH₄/MoS₂ systems and CH₄/MoSe₂ systems, and the energy band gap of four systems were observed along the gamma point (G) was noticed to be 1.261 eV (MoTe₂), 0.852 eV (MVTe), 0 eV (VMo), and 0.316 eV (MV_D). One of the strangest things of all was the defect of the Mo atom, which allowed the system to be transformed from semiconductor to metal. Meantime, the DOS (Fig. 6) also showed that the Te atoms in MoTe₂ had four peaks value, the peak was -10 eV, -5 eV, -3 eV, and -1 eV and the Mo atom in MoSe₂ had overlapping peaks at about 1 eV.

In general, on the basis of the adsorption behaviors of CH₄ gas molecule in different systems, the CH₄ gas molecule adsorbed by the MV_X could have two peaks near the Fermi level. The DOS between the two spikes was not zero but very wide, which reflected the strong covalent

property of the system. To summarize all the data, the MV_{Te} might become an ideal sensing material for the detection of CH₄ gas molecule.

Conclusions

We carried out density-functional-GGA studies to study the interaction of an isolated CH₄ gas molecule on MoX₂ (X=S, Se, Te). The results indicated that the different defects changed the electrical properties of MoX₂ greatly, and our results revealed a weak interaction between the CH₄ gas molecules and MoX₂ monolayer, which indicated the physical nature of the adsorption. The total electron density plots confirmed the physisorption of gas molecules on the MoX₂ surface, as the material weakly interacts with the CH₄ gas molecules without the formation of covalent bonds at the interface region. Furthermore, the structure of MV_D has a good band

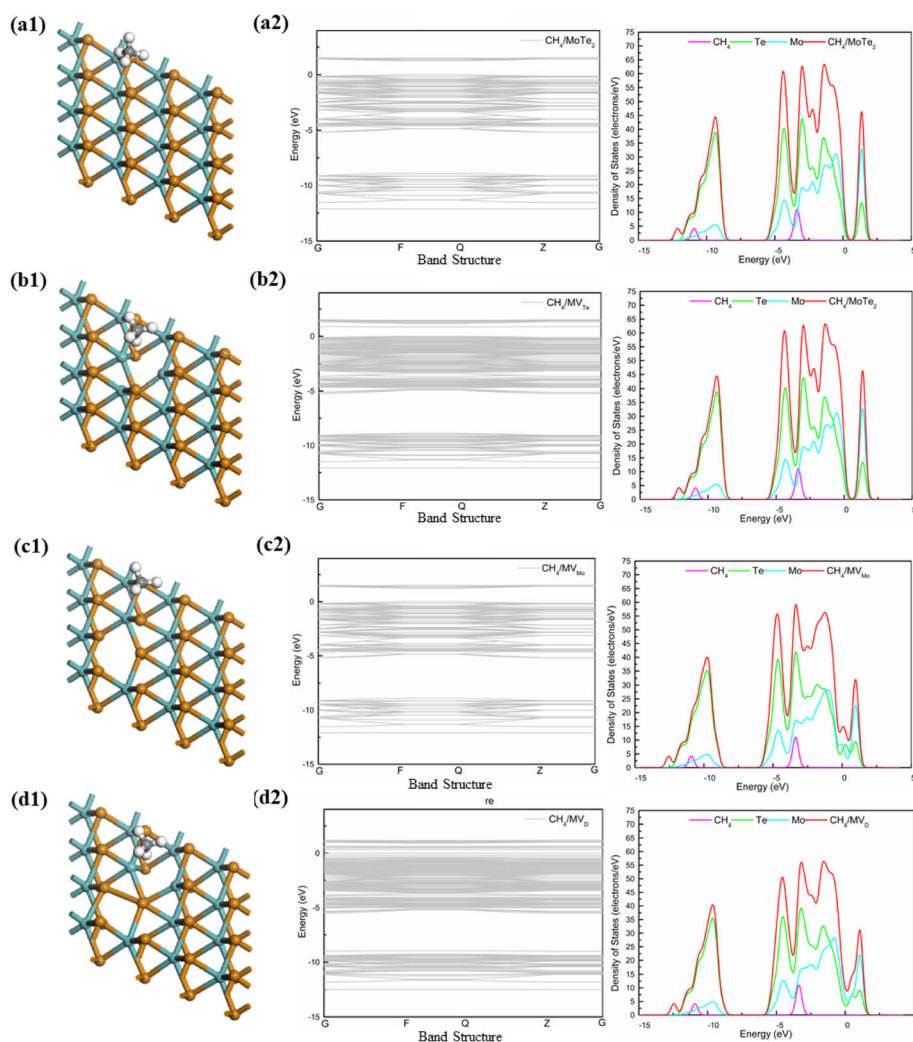


Fig. 6 The structure and DOS of CH₄ gas molecule on four systems (MoTe₂, MV_{Te}, MV_{Mo} and MV_D)

gap, semiconductor property, the best adsorption energy, and the stronger charge transfer for the CH₄ gas molecule. Besides, the electronic band structures of the sensing system were altered upon the adsorption of gas molecules. MoTe₂ had the highest adsorption energy (−0.51 eV), the shortest intermolecular distance (2.20 Å), and the higher charge transfer (−0.026 e). At last from the analysis of these three materials, it could be seen that MV_D (MoTe₂) had the best adsorption effect on CH₄ gas molecule. The calculated results thus suggested a theoretical basis for the potential application of MV_D(MoTe₂) monolayers in the CH₄ based gas sensor devices.

Abbreviations

CH₄: Methane; DOS: Density of states; Ea: Adsorption energy

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Authors' Contributions

JR and YX designed and carried out the experiments and drafted the manuscript. JR, HL, and LW participated in the work to analyze the data. HL participated in the revision of the manuscript. All authors read and approved the final manuscript.

Authors' information

Not applicable

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Availability of Data and Materials

All data are fully available without restriction.

Competing Interests

The authors declare that they have no competing interests.

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References

- Wetchakun K, Samerjai T, Tamaekong N et al (2011) Semiconducting metal oxides as sensors for environmentally hazardous gases [J]. *Sens Actuators B* 160(1):580–591
- Abbasi A, Sardroodi JJ (2016) N-doped TiO₂ anatase nanoparticles as a highly sensitive gas sensor for NO₂ detection: insights from DFT computations [J]. *Environ Sci: Nano* 3(5):1153–1164
- Ueda T, Bhuiyan MMH, Norimatsu H et al (2008) Development of carbon nanotube-based gas sensors for NOx gas detection working at low temperature [J]. *Physica E: Low-dimensional Systems and Nanostructures* 40(7):2272–2277
- Abbasi A, Sardroodi JJ (2016) Theoretical study of the adsorption of NOx on TiO₂/MoS₂ nanocomposites: a comparison between undoped and N-doped nanocomposites[J]. *J Nanostruct Chem*
- Abbasi T, Abbasi SA (2011) 'Renewable'hydrogen: prospects and challenges [J]. *Renew Sustain Energy Rev* 15(6):3034–3040
- Reddy RG (2006) Fuel cell and hydrogen economy [J]. *J Mater Eng Perform* 15(4):474–483
- Cheng X, Shi Z, Glass N et al (2007) A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation [J]. *J Power Sources* 165(2):739–756
- Novoselov KS, Morozov SV, Mohinddin TMG et al (2010) Electronic properties of graphene [J]. *Physica Status Solidi* 244(11):4106–4111
- Jose D, Datta A (2013) Structures and chemical properties of silicene: unlike graphene [J]. *Acc Chem Res* 47(2):593–602
- Hasan MZ, Kane CL (2010) Colloquium: topological insulators [J]. *Rev Mod Phys* 82(4):3045
- Stankovich S, Dikin DA, Dommett GHB et al (2006) Graphene-based composite materials [J]. *Nature* 442(7100):282
- Nijamudheen A, Bhattacharjee R, Choudhury S et al (2015) Electronic and chemical properties of germanene: the crucial role of buckling [J]. *J Phys Chem C* 119(7):3802–3809
- Chowdhury C, Jahiruddin S, Datta A (2016) Pseudo-Jahn–Teller distortion in two-dimensional phosphorus: origin of black and blue phases of phosphorene and band gap modulation by molecular charge transfer [J]. *J Phys Chem Lett* 7(7):1288–1297
- Bhattacharjee R, Majumder T, Datta A (2019) Analysis of pseudo jahn–teller distortion based on natural bond orbital theory: case study for silicene [J]. *J Comb Chem*
- Ni J, Yang B, Jia F et al (2018) Theoretical investigation of the sensing mechanism of the pure graphene and Al, B, N, P doped mono-vacancy graphene-based methane[J]. *Chem Phys Lett* 710:221–225
- Qiao X, Chao Z, Shao Q et al Structural characterization of corn stover lignin after hydrogen peroxide presoaking prior to ammonia fiber expansion pretreatment [J]. *Energy Fuels*, 2018: acs.energyfuels. 8b00951
- Zhao C, Yan C, Ma Z et al (2017) Optimization of liquid ammonia pretreatment conditions for maximizing sugar release from giant reed (*Arundo donax* L.) [J]. *Biomass Bioenergy* 98(2):61–69
- Zhao C, Shao Q, Ma Z et al (2016) Physical and chemical characterizations of corn stalk resulting from hydrogen peroxide presoaking prior to ammonia fiber expansion pretreatment [J]. *Ind Crops Prod* 83(2):86–93
- Zhao C, Qiao X, Cao Y et al (2017) Application of hydrogen peroxide presoaking prior to ammonia fiber expansion pretreatment of energy crops. *Fuel* 205:184–191
- Mak KF, Lee C, Hone J et al (2010) Atomically thin MoS₂: a new direct-gap semiconductor [J]. *Phys Rev Lett* 105(13):136805
- Pan H, Zhang YW (2012) Edge-dependent structural, electronic and magnetic properties of MoS₂ nanoribbons [J]. *J Math Chem* 22(15):7280–7290
- Ataca C, Sahin H, Ciraci S (2012) Stable, single-layer MX₂ transition-metal oxides and dichalcogenides in a honeycomb-like structure [J]. *J Phys Chem C* 116(16):8983–8999
- Pan H, Zhang YW (2012) Tuning the electronic and magnetic properties of MoS₂ nanoribbons by strain engineering [J]. *J Phys Chem C* 116(21):11752–11757
- Yin Z, Li H, Li H et al (2011) Single-layer MoS₂ phototransistors [J]. *ACS Nano* 6(1):74–80
- Frindt RF (1966) Single crystals of MoS₂ several molecular layers thick [J]. *J App Phys* 37(4):1928–1929
- Joensen P, Frindt RF, Morrison SR (1986) Single-layer MoS₂ [J]. *Mater Res Bull* 21(4):457–461
- Li Y, Zhang X, Chen D et al (2018) Adsorption behavior of COF₂ and CF₄ gas on the MoS₂ monolayer doped with Ni: A first-principles study [J]. *App Surf Sci* 443:274–279
- Haldar S, Vovusha H, Yadav MK et al (2015) Systematic study of structural, electronic, and optical properties of atomic-scale defects in the two-dimensional transition metal dichalcogenides MX₂ (M= Mo, W; X= S, Se, Te) [J]. *Phys Rev B* 92(23):235408
- Cha J, Sung D, Min KA et al (2018) Van der Waals density functional theory study of molecular adsorbates on MoX₂ (X= S, Se or Te) [J]. *J Korean Phys Soc* 73(1):100–104
- Li H, Huang M, Cao G (2016) Markedly different adsorption behaviors of gas molecules on defective monolayer MoS₂: a first-principles study [J]. *Phys Chem Chem Phys* 18(22):15110–15117
- Lee C, Hone J, Shan J et al (2010) Atomically 392 Thin MoS₂: A new direct-gap semiconductor [J]. *Phys. Rev. Lett* 393(105):136805
- Ma D, Wang Q, Li T et al (2016) Repairing sulfur vacancies in the MoS₂ monolayer by using CO, NO and NO₂ molecules [J]. *J Mat Chem C* 4(29): 7093–7101
- Shokri A, Salami N (2016) Gas sensor based on MoS₂ monolayer[J]. *Sens Actuators B* 236:378–385
- Yue Q, Shao Z, Chang S et al (2013) Adsorption of gas molecules on monolayer MoS₂ and effect of applied electric field [J]. *Nanoscale Res Lett* 8(1):425
- Zhao S, Xue J, Kang W (2014) Gas adsorption on MoS₂ monolayer from first-principles calculations [J]. *Chem Physics Lett* 595:35–42
- Ray SJ (2016) First-principles study of MoS₂, phosphorene and graphene based single electron transistor for gas sensing applications [J]. *Sens Actuators B: Chem* 222:492–498
- O-T W J. Molecular mechanics: by U. Burkert and N. L. Allinger, American Chemical Society, Washington. *Journal of Molecular Structure Theochem* [J],109(3–4) (1984) 401–401.
- Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects [J]. *Phys Rev* 140(4A):A1133
- Perdew JP (1997) JP Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 78, 1396 (1997) [J]. *Phys. Rev. Lett.* 78:1396
- Monkhorst HJ, Pack JD (1976) Special points for Brillouin-zone integrations [J]. *Phys Rev B* 13(12):5188
- Becke AD (1993) A new mixing of Hartree–Fock and local density-functional theories [J]. *J Chem Phys* 98(2):1372–1377
- Komsa HP, Krashennnikov AV (2015) Native defects in bulk and monolayer MoS₂ from first principles [J]. *Phys Rev B* 91(12):125304
- Zahid F, Liu L, Zhu Y et al (2013) A generic tight-binding model for monolayer, bilayer and bulk MoS₂ [J]. *Aip Advances* 3(5):052111
- Sharma M, Jamdagni P, Kumar A et al (2016) Interactions of gas molecules with monolayer MoSe₂: A first principle study [C]//AIP Conference Proceedings. AIP Publishing 1731(1):140045
- Fan Z, Wei-Bing Z, Bi-Yu T (2015) Electronic structures and elastic properties of monolayer and bilayer transition metal dichalcogenides MX₂ (M= Mo, W; X= O, S, Se, Te): a comparative first-principles study [J]. *Chinese Physics B* 24(9):097103

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